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Dissociation energy of NbN molecule from potential energy curves

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The evaluation of dissociation energies of diatomic molecules is of fundamental importance in thermochemistry, astrophysical problems and chemical physics etc. Since there is no report of either dissociation energy or potential energy curves for known electronic states of NbN molecule, present work has been undertaken.

Recently Pazyuk *et al* (1986) studied the absorption spectrum of $A^3\Phi - X^3\Delta$ transition for NbN molecule using the interacavity laser excitation. Emission spectrum of the NbN molecule was earlier studied by Dunn and Rao (1969), who analysed the $A^3\Phi_3 - X^3\Delta_2$ sub-band. The other two sub-bands are having very dense structure due to large nuclear hyperfine structure present in $X^3\Delta$ state. Green *et al* (1973) also studied the IR spectra of NbN molecule by trapping it in an Argon matrix. Pazyuk *et al* (1986) photographed the spectra of NbN in high resolution and analysed 48 bands belonging to three subsystems of $^3\Phi - ^3\Delta$ transition.

There are various methods to estimate the dissociation energies of molecules. One of them is from potential energy curves. The Morse (1929), Hulburt-Hirschfelder (H-H) (1941), Lippincott (Steel and Lippincott 1961) and electronegativity (Szoke and Baitz 1968) etc. potential functions are widely used for such purpose. If reliable spectroscopic data is available, the potential energy curves of corresponding electronic states of a molecule can be constructed and the dissociation energy can be estimated using the curve fitting method.

The RKRV curves (Rydberg 1931, Klein 1932, Rees 1947, Vanderslice *et al* 1959) are constructed for the $X^3\Delta$ and $A^3\Phi$ states of NbN by using the molecular constants derived by Pazyuk *et al* (1986) which are reported in Table 1 and the turning points are reported in Table 2.

In the present case the H-H (Hulbert and Hirschfelder 1941), Tietz (1971) and Mattera *et al*'s (1980) potential functions are used. They are as follows.

(i) Hulburt-Hirschfelder (1941) function is :

$$U_{HH}(r) = D_e\{(1-e^{-x})^2 + cx^3e^{-3x}(1+bx)\} \qquad (1)$$

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Table 1. Molecular constants of NbN molecule.

State	w_e (cm^{-1})	$w_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e^* (cm^{-1})	r_e (Å)
$X^3\Delta$	1043.9	4.18	0.4993	0.002713	1.6656
$A^3\Phi$	994 2	4.27	0.4941	0.002857	1.6743

*From Pekeris relation.

Table 2. RKR turning points and U values of NbN molecule calculated using different potential functions.

	$X^3\Delta$ state					$A^3\Phi$ state	
v	U_{RKR} cm^{-1}	r_{min} r_{max} Å	U_{H-H} $D_e=65200$ cm^{-1}	U_{TZ} $D_e=64750$ cm^{-1}	U_{MT} $D_e=65200$ cm^{-1}	U_{RKR} cm^{-1}	r_{min} r_{max} Å
0	520.90	1.6166 1.7198	514.92 526.23	511.70 523.01	511.90 526.24	496.03	1.6242 1.7300
1	1556.44	1.5831 1.7625	1548.58 1564.58	1541.10 1557.71	1548.54 1564.53	1481.69	1.5901 1.7739
2	2583.62	1.5613 1.7937	2573.14 2594.78	2564.11 2588.03	2573.05 2594.78	2458.81	1.5678 1.8061
3	3602.44	1.5443 1.8201	3587.96 3612.17	3579.91 3609.51	3587.85 3612.12	3427.39	1.5505 1.8334
4	4612.90	1.5300 1.8439	4600.73 4625.20	4596.13 4630.67	4600.58 4624.97	4387.43	1.5360 1.8580
5	5615.00	1.5176 1.8658	5604.84 5625.28	5606.00 5642.96	5604.66 5625.05	5338.93	1.5234 1.8808
6	6608.74	1.5066 1.8865	6599.29 6621.32	6608.39 6655.53	6599 05 6621.14	6281.89	1.5122 1.9022
7	7594.12	1.4966 1.9061	7592.32 7603.00	7611.61 7657.92	7592.06 7602 71	7216.31	1.5022 1.9226
8	8571.14	1.4875 1.9250	8573.07 8579.61	8604.41 8659.63	8572 81 8579.42	8142.19	1.4996 1.9488

where

$$x = \alpha(r - r_e) \; ; \; \alpha = \frac{w_e}{2(B_e D_e)^{\frac{1}{2}} r_e}$$

$$c = 1 + a_1 \left(\frac{D_e}{a_0}\right)^{\frac{1}{2}}$$

$$b = 2 - \left[\frac{7}{12} - \frac{D_e a_2}{a_0}\right] \Big/ c$$

a_0, a_1, a_2 are Dunham coefficients.

D_e is the dissociation energy. Other constants have their usual meaning.

(ii) The Tietz (1971) potential function is :

$$U_{TZ}(r) = D_e\left(\frac{r-r_e}{r}\right)^2 \left\{ \frac{\Delta\left(1+\frac{Hr_e}{F}\right) - \frac{Hr_e}{F} + \frac{Hr_e}{F}(r/r_e)}{1+\frac{Hr_e}{F}(r/r_e)} \right. , \tag{2}$$

where Δ is Sutherland parameter, a dimensionless quantity and expressed in terms of force constants k_e as

$$\Delta = k_e r_e^2/2D_e \; ; \; Hr_e/F = \Delta(F_e - 1)/(2\Delta - \Delta F_e - 1)$$

where

$$F_e = (\alpha_e w_e^2)/6B_e^2$$

The above potential function was used to estimate the dissociation energies of AlBr, BiF, BeF and IO molecules by Rai et *al* (1972). Besides its efficiency to represent the true potential energy curves to a good extent, the Schrödinger equation is also solvable for this potential function.

(iii) Mattera et *al* (1980) have suggested the potential function as

$$U_{MT}(r) = D_e\left\{1 - \left[1+\frac{\gamma(r-r_e)}{pr_e}\right]^{-p}\right\}^2 \tag{3}$$

where

$$p = (12a_2 - 11a_1^2)/(7a_1^2 - 12a_2) \; ; \; \gamma = \frac{-a_1}{1+(1/p)}$$

a_1 and a_2 are Dunham coefficients.

Under suitable condition this function includes the most popular curves. In fact, if the quantity in curly bracket of eq. (3) is defined as $f(x)$, the potential suggested by Mattera et *al* (1980) is

$$U_{MT}(x) = D_e[f(x)]^2[1 + d_1 f(x) + d_2 f^2(x) + \ldots] \tag{4}$$

where

$$x = r - r_e$$

and

$$f(x) = 1 - \left(1+\frac{\gamma x}{p}\right)^{-p}$$

d_1, d_2, d_3... could be determined in terms of Dunham coefficients, a_i by equating the derivatives at $x = 0$ of $U_{MT}(x)$. First few di's are listed by Mattera et *al* (1980).

For calculations of dissociation energy usually first term of eq. (4) is sufficient, as the contribution due to cubic and higher terms is too small and can be neglected.

The RKRV curves to both the states are constructed for the first nine levels from $V=0$ to 8. By substituting the values of r_{min}, r_{max} and appropriate constants of respective potential functions; the D_e values are calculated using curve fitting method. The accurate D_e values using H-H (Hulbert and Hirschfelder 1941), Tietz (1971) and Mattera *et al* (1980) potential functions, are 65199.38 ± 298.65, 64742.26 ± 442.88 and 65200.72 ± 299.35 cm^{-1} respectively. The U values obtained using these best-fits for respective potential function with corresponding D_e values, are also shown in Table 2. Since H-H and Mattera *et al* potential functions give the D_e values almost same, the D_e value is estimated as 65200 cm^{-1}. D_0^0 comes out to be 8.02 eV.

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